Thermodynamics of Neptunium (V) Complexes with Phosphate at Elevated Temperatures

Yuanxian Xia[1*], Judah I. Friese[1], Paula P. Bachelor[1], Dean A. Moore[1], Linfeng. Rao[2]

1. Pacific Northwest National Laboratory, P. O. Box 999, Richland, WA 99352
2. Lawrence Berkeley National Laboratory, Berkeley, CA 94720

Abstract – The complexation of Np(V) with phosphate at elevated temperatures has been studied by a synergistic extraction method. A mixed buffer solution of TRIS and MES was used to maintain an appropriate pH value during the distribute experiments. The distribution ratio of Np(V) between the organic and aqueous phases was found to decrease as the concentrations of phosphate were increased. Stability constants of the 1:1 and 1:2 Np(V)-HPO_4^{2-} complexes, dominant in the aqueous phase under the experimental conditions, were calculated from the effect of [HPO_4^{2-}] on the distribution ratio. The thermodynamic parameters including enthalpy and entropy of complexation between Np(V) and HPO_4^{2-} at 25° C- 55° C were calculated by the temperature coefficient method.
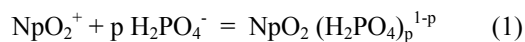

INTRODUCTION

Neptunium is one of the radionuclides of concern in the post-closure chemical environment in the proposed Yucca Mountain repository due to its high toxicity and very long half life (^{237}Np, $t_{1/2}$ = 2.14x10^6 years) as well as its high abundance in the nuclear waste. The fractional dose attributed to ^{237}Np will reach 67% at 75,000 years[1]. As a result, the migration of neptunium in the post-closure chemical environment of waste repositories and the surrounding geologic media is of great concern to long-term repository performance. Np(V) is the most stable oxidation state under environmental and nuclear waste conditions where O_2 overpressure is approximate 20%[1]. The solubility of neptunium after disposal will depend largely on its reactions (e.g., dissolution/precipitation and complexation) with various components present in the repository. The interactions of actinides with some inorganic ligands at elevated temperatures may be a significant factor in determining the solubility and migration of the actinides in the nuclear waste repository. For example, phosphate is expected to be present in the water in contact with the nuclear waste packages and affect the speciation and migration of actinides by forming complexes[1-2]. Studies of complexation of Np(V) with various inorganic ligands have recently reviewed[3]. There have been several studies of the aqueous Np(V) - phosphate system using spectrophotometric[4], ion exchange[5-6], solvent extraction[7] or co-precipitation methods[8]. But all these data on the stability constants of Np(V) complexes with phosphate were obtained at the
*E-mail: **yuanxian.xia@pnl.gov**

room temperature. Only Rees and Danie[6] reported their data on the stability constants of Np(V) complexes with HPO_4^{2-} at different temperatures (10, 25 and 35° C). In fact, no data are available in the Np(V)-HPO_4^{2-} system at temperatures > 35°C in the literature. It is well known that the equilibrium constants of complexation could vary by orders of magnitude in the temperature range (25-80° C) relevant to waste repositories. In order to minimize the uncertainty in the prediction of Np(V) migration, it is necessary to know sufficient and reliable thermodynamic data on its complexes at elevated temperatures. Unfortunately, experimental data on the effects of temperatures in these systems are very scarce at present.

In this work, a solvent extraction method[9-11] was used to determine the stability constants of Np(V) complexes with phosphate anions at I = 1.0 M $NaClO_4$ and t = 25° - 55° C. It is expected that HPO_4^{2-} anion is the dominant species in the aqueous phase at pcH (= -log [H$^+$]) about 7.4. A synergist of trioctyl phosphine oxide (TOPO) and 2-thenoyltrifluoroacetone (TTA) was used as a solvent extractant and toluene as a solvent.

In the system of Np(V)-phosphate complexes, there is possibility of the formation of different species of complexes. The complex reactions of Np(V) with $H_2PO_4^-$ and HPO_4^{2-} anions under experimental conditions used in this study can be expressed as (species PO_4^{3-} can be neglected):

$$NpO_2^+ + p\ H_2PO_4^- = NpO_2\ (H_2PO_4)_p^{1-p} \qquad (1)$$

$$NpO_2^+ + q\ HPO_4^{2-} = NpO_2\ (HPO_4)_q^{1-2q} \qquad (2)$$

with the overall stability constants β_p and β_q defined as:

$$\beta_p = [NpO_2(H_2PO_4)_p^{1-p}]/([NpO_2^+][H_2PO_4^-]^p) \qquad (3)$$

$$\beta_q = [NpO_2(HPO_4)_q^{1-2q}]/([NpO_2^+][HPO_4^{2-}]^q) \qquad (4)$$

In the solvent extraction system, the distribution ratio (D) of a metal ion, M, is defined as:

$$D = \Sigma\,[M]_o\,/\Sigma\,[M]_a \qquad (5)$$

Where $\Sigma\,[M]_o$ is total concentration of metal ion in the organic phase assuming there is only a single organic (o) phase, $\Sigma\,[M]_a$ is total concentration of metal ion in the aqueous phase and there are various species in the aqueous phase (a). The equation (5) can be written, with the stability constants as expressed in the literature[9-11]:

$$D_o/D = 1 + \Sigma\,\beta_p[L_p]^p + \Sigma\,\beta_q[L_q]^q \qquad (6)$$

Where D_o is the distribution ratio in the absence of complexation in the aqueous phase. For the Np(V)-phosphate complex system at a fixed pcH (about 7.4), M, L_p, L_q stand for Np(V), $H_2PO_4^-$, HPO_4^{2-}, respectively. TOPO with TTA anion as a synergistic extractant, toluene as a solvent.

EXPERIMENTAL

Reagents and solutions

All solutions were prepared with distilled-deionized (DDI) water and all reagents used in this work were analytical grade or higher. The stock solutions of 1.0 M, 2.0 M $NaClO_4$ (Aldrich) and 0.1 M Na_2HPO_4 (Aldrich) were prepared by dissolving appropriate amounts of these reagents in DDI water. Sodium perchlorate (Aldrich) was used for ionic strength adjustment without further purification. Perchloric acid (Aldrich) and NaOH (1.0 N standard, Aldrich) were used to adjust pH. Buffer reagents of morpholinoethanesulfonic acid (MES, Alfa Aesar) and tri-hydroxy-methylaminomethane (TRIS, Alfa Aesar) were used to maintain pcH at about 7.4 in the aqueous solution. Sodium bromate (Aldrich) and $NaNO_2$ (Aldrich) were used for oxidizing and reducing neptunium, respectively, during the preparation of stock solution of NpO_2^+. A mixture of 0.027 M TTA (Aldrich) and 0.028 M TOPO (Aldrich) in toluene (Aldrich) was used as a synergistic extractant. TTA was purified by vacuum sublimation at 42° C. TOPO was used without further purification. The organic solutions were pre-equilibrated with the aqueous stock solution of 1.0 M $NaClO_4$ and

stored in a dark glass bottle. All solutions except the Np(V) tracer solution were filtered with a 0.2 μm microfiltration system to minimize sorption of Np(V) by suspended particles in solution.

A Np(V) stock solution was prepared using the procedure described in the literature[12]. A small amount of solid $NaBrO_3$ was added to a solution of neptunium in 1.0 M $HClO_4$ and the solution warmed to facilitate the oxidation of neptunium to Np(VI). Then a small amount of $NaNO_2$ was added to this solution causing a change in color from pink to green, indicating the reduction of NpO_2^{2+} to NpO_2^+. Finally, the NpO_2^+ species was precipitated by adding 1.0 M NaOH to the solution. The $NpO_2(OH)$ precipitate was washed several times with DDI water and dissolved with 0.1 M $HClO_4$. The oxidation state of Np(V) was confirmed spectrophotometrically on a Cary 500 UV-Vis-NIR Spectrophotometer. From the stock solution, a working solution of Np(V) was prepared in 0.06 N $HClO_4$. The activity of ^{237}Np in the samples was measured on a Wallac (Model 1414) liquid scintillation counter (LSC). The β-activity of ^{233}Pa, the daughter nuclide of ^{237}Np, was automatically discriminated.

Temperature-controlled extraction equipment

The temperature-controlled extraction equipment used for this work has been described in a previous paper[13]. To shake the samples at the desired temperature, a reaction block with the heat tape or a block heater was used. Temperature control was accomplished through the block heater's temperature control or through a variable-voltage transformer when using the heat tape.

A Speedfuge (HSX10K) centrifuge with a water jacket enclosed around the rotor was used to centrifuge the samples. Water from a Brinkmann RM6 Lauda temperature controlled water circulator controlled the temperature of the samples inside the centrifuge.

Temperature adjusted reaction blocks are used to maintain the temperature of experimental solutions, samples, and pH buffers.

Determination of H^+ concentrations

A Corning 355 pH meter was used with a combination glass electrode (Ross Orion) to measure the pH. Because the pH was measured in the sodium perchlorate solution, the inner solution (3 M KCl) of the electrode was replaced with a saturated NaCl solution to avoid erratic electrode performance. The electrode was calibrated with 4.00, 7.00 and 10.00 pH buffer standard solutions at the same elevated temperature as the reaction block. The pH meter readings (pH_m) were converted to hydrogen concentration (pcH = - log [H^+]) using the following

calibration equation proposed by Irving et al.[14]:

$$pcH = pH_m + b \qquad (7)$$

Where b is the correction factor depending on the solution composition. For example, b = 0.27 in 1.0 M NaClO$_4$[9-10].

Calculation of dissociation constants of phosphoric acid

The free concentration of phosphate anion in each extraction vial was calculated from the measured pH (converting pcH), the total concentration of Na$_2$HPO$_4$ and the dissociation constants of phosphoric acid at the respective temperatures and ionic strength 1.0 M NaClO$_4$. Because Np(V) is at the tracer level and the amount of Np(V)- HPO$_4^{2-}$ complex is negligible compared to the total amount of [HPO$_4^{2-}$]$_T$. The concentration of free HPO$_4^{2-}$ anion ([HPO$_4^{2-}$]$_f$) can be calculated by using the equation (8):

$$[HPO_4^{2-}]_f = [HPO_4^{2-}]_T /(1+ [H^+]/K_{a2} + [H^+]^2/K_{a1}K_{a2}) \qquad (8)$$

Where K$_{a1}$ and K$_{a2}$ are the first and second dissociation constants of phosphoric acid, respectively. No data at high temperatures (such as 40°C and 55°C) and ionic strength (1.0 M NaClO$_4$) are available in the literature. The K$_{a1}$ and K$_{a2}$ were calculated based on the literature data at zero ionic strength and different temperatures[15-16] by using Specific Ion Interaction Theory (SIT)[17]. In the SIT approach, such as the following protonation reaction:

$$H^+ + L_q^{2-} = L_p^- \qquad (9)$$

Where as above mentioned L$_q^{2-}$ and L$_p^-$ stand for HPO$_4^{2-}$ and H$_2$PO$_4^-$, respectively. The equilibrium constant of above reaction at zero ionic strength K$_2^o$, is related to the constant K$_2$ at ionic strength I$_m$ (in molality) by

$$\log K_2 = \log K_2^o + \Delta Z^2 D - \Delta \varepsilon I_m \qquad (10)$$

Where $\Delta Z^2 = Z_p^2 - Z_H^2 - Z_q^2 = -4$, D is the Debye-Hückel term:

$$D = 0.509 I_m^{1/2}/ (1 + aB I_m^{1/2}) \qquad (11)$$

$$\Delta \varepsilon = \varepsilon_{Lp} - \varepsilon_H - \varepsilon_{Lq} = -0.21^{18} \qquad (12)$$

with Z being the charge on the designated species, ε is interaction parameter for each cation-anion pair and aB = 1.5 as suggested by Scatchard[19].

Similar to above approach, the equilibrium constant K$_1$ (H$^+$ + H$_2$PO$_4^-$ = H$_3$PO$_4$) values at the different temperatures were obtained by using SIT. The

dissociation constants, pK$_{a1}$ (= - log K$_{a1}$ = log K$_1$) and pK$_{a2}$ (= - log K$_{a2}$ = log K$_2$), of phosphoric acid at different temperatures and at fixed ion strength of 1.0 M NaClO$_4$ listed in Table 1.

Synergistic extraction

The distribution experiments were conducted following the procedure described in the literature[9-11]. For each extraction experiment, 1.5 ml of 1.0 M NaClO$_4$ aqueous solution that contained desired amounts of Na$_2$HPO$_4$ at appropriate pH was mixed with an equal volume of 0.027 M TTA with 0.0028 M TOPO in toluene in a borosilicate glass vial. After addition of 10 μL ^{237}Np(V) tracer, the vials were inserted into the temperature-controlled reaction block and shaken for two hours at the desired temperature. Kinetic studies confirmed that the extraction equilibrium was achieved in less than one hour. The vials were centrifuged at the same temperature as the reaction block on the shaker and aliquots of 0.5 ml were taken from each phase to measure the α-activity by LSC using OPTI Fluor as the scintillation cocktail. The remaining aqueous phase was used for pH measurement at the same temperature as the reaction block on the shaker.

RESULTS AND DISCUSSION

Np(V)-HPO$_4^{2-}$ complexes

A series of experiments with constant pcH were conducted at an ionic strength of 1.0 M NaClO$_4$. Distribution ratios (D) of Np(V) in the organic and aqueous phases were found to decrease with the increase in the concentration of Na$_2$HPO$_4$. A complete set of the extraction data at different temperatures are listed in Tables 2-4. The decrease in D can be attributed to the increase in concentration of Np(V)- HPO$_4^{2-}$ complexes in the aqueous phase that are not extracted by TOPO+TTA. Stability constants of the 1:1 and 1:2 Np(V)-HPO$_4^{2-}$ complexes, dominant in the aqueous phase under the experimental conditions, were calculated from the effect of [HPO$_4^{2-}$] on the distribution ratio.

Experiments have been conducted at 25°C, 40°C and 55°C. A representative plot of D$_o$/D versus the free concentration of HPO$_4^{2-}$ at 40 ± 1°C is shown in Figure 1, where the points are experimental data and the solid line represents the fit for the formation of 1:1 and 1:2 complexes. From these data, the stability constants of Np(V) complexes with HPO$_4^{2-}$ at 25 - 55°C are calculated.

Literature data indicate that the hydrolysis of Np(V) is insignificant when pcH < 8 in the temperature range of 10-85°C[20]. Since the experiments in this study were

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conducted at pcH ~7.4, the hydrolysis reactions of Np(V) are not included in the calculation.

The apparent stability constants obtained from this work are listed in Table 5 along with some literature data for comparison. The values at 25° C from this work (log β_{101} = 2.32, log β_{102} =3.78) are consistent with that in the literature data (see Table 5). The values at 40° C and 55° C from this work are the first experimental values to be reported. The results show that the stability constant of 1:1 complex between Np(V) and HPO_4^{2-} is decreased at higher temperatures. The tendency of the changing of stability constants with temperatures is similar to the literature data obtained from the temperatures from 10° C to 35° C[6] (see Table 5). No stability constants of the 1:2 Np(V)-HPO_4^{2-} complex at elevated temperatures are available in the literature. The data obtained from this study indicate that the stability constants of 1:2 Np(V)-HPO_4^{2-} complex, are increased at higher temperatures (see Table 5).

As above mentioned, in the system of Np(V)-phosphate complexes, there is possibility of the formation of different species of complexes including the complex reactions of Np(V) with $H_2PO_4^-$ anions under experimental conditions used in this study. Therefore, during the calculation of stability constants of Np(V) with HPO_4^{2-} complexes involved the stability constants of Np(V) with $H_2PO_4^-$ complexes at different temperatures obtained from our previous data[21] (see table 5). The following equation (13), derived from eq. (6) with the second dissociation constant, was used for corrected the stability constants:

$$\beta_q = \mathbf{\beta_q} - \beta_p \ [H^+]/K_{a2} \qquad (13)$$

where β_q is corrected stability constant, $\mathbf{\beta_q}$ is fit data based on the experimental data in this study. The results show that both values of $\mathbf{\beta_q}$ and β_q are not significant different under the experimental conditions of this study.

Effect of temperature on stability constants

The effect of temperature on the stability constants of the Np(V)- HPO_4^{2-} complexes was evaluated at the range of temperature from 25° to 55° C. By using the Van't Hoff equation, we automatically assume that the enthalpy of complexation remains constant and an "average" enthalpy of complexation for this temperature range can be calculated. From the determined stability constants listed in the Table 5, the corresponding values of $\Delta G^{o'}$, $\Delta H^{o'}$, and $\Delta S^{o'}$ were calculated according to equation (14) and (15):

$$\Delta G^{o'} = - RT \ln \beta \qquad (14)$$

$$\partial \ln \beta / \partial (1/T) = - \Delta H^{o'}/R \ ; \quad \Delta S^{o'} = (\Delta H^{o'} - \Delta G^{o'})/T \qquad (15)$$

The calculated thermodynamic parameters are listed in Table 6. The results indicate that for the complex formation of $NpO_2 (HPO_4)^-$ the values of $\Delta H^{o'}$ and $\Delta S^{o'}$ are negative enthalpy which reflects no dehydration energy required to form complexes and supports the interpretation out sphere binding for the Np(V) complexes with HPO_4^{2-} [22-24]. While the enthalpy for the complex formation of $NpO_2 (HPO_4)_2^{3-}$ is positive and relatively large indicating the complex reactions are entropy-driven. The positive enthalpy reflects the dehydration energy required for forming complexes and supports the interpretation of inner sphere binding for the Np(V) complexes with HPO_4^{2-} [22-24]. These parameters should be helpful in predicting of the effect of temperature on the complexation of Np(V) with phosphate at elevated temperatures.

CONCLUSIONS

Stability constants of the Np(V) with HPO_4^{2-} complexes were measured in aqueous solutions with 1.0 M $NaClO_4$ as the background electrolyte at pcH ~7.4 and at various temperatures (from 25 to 55° C) by using synergistic extraction technique. Under the experimental conditions of this study, the 1:1 and 1:2 complexes ($NpO_2HPO_4^-$ and $NpO_2(HPO_4)_2^{3-}$) were found to be the dominant species. The stability constants of 1:1 Np(V)-HPO_4^{2-} complexes are decreased with increasing temperature, consistent with a negative enthalpy of complexes and the out sphere complexes. While the stability constants of 1:2 Np(V)- HPO_4^{2-} complexes are increased with increasing temperature that are consistent with a positive enthalpy and the inner sphere complexes. These results have demonstrated that the temperature has a significant effect on the complexation of Np(V) with $HPO4^{2-}$ and it is important to conduct studies to evaluate the temperature effect to help predict the migration of neptunium in the high-level waste and in the proposed Yucca Mountain repository where temperature could be higher than the ambient temperature.

ACKNOWLEDGEMENTS

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Table 1. The dissociation constants of phosphoric acid at the different temperatures and
fixed ionic strength of 1.0 M NaClO$_4$

Temperature (^{o}C)	Ionic Strength	pK$_{a1}$	pK$_{a2}$	Reference
25	1.0 M NaClO4	1.780	6.595	18
40	1.0 M NaClO4	1.841	6.558	18
55	1.0 M NaClO4	1.926	6.539	18

The pK$_{a1}$ (= - log K$_{a1}$) at different temperatures and I=1.0 M NaClO$_4$ obtained from the
literature data pK$_{a1}$[16] = 2.124 (25 ^{c}o, I = 0), 2.198 (40 ^{o}C, I = 0) and 2.294 (55 ^{o}C, I = 0) by
using SIT approach.

The pK$_{a2}$ (= - log K$_{a2}$) at different temperatures and I=1.0 M NaClO$_4$ obtained from the
literature data pK$_{a2}$[15] by using SIT approach.

Table2. Solvent extraction data for the synergistic extraction system of Np(V)-HPO$_4{}^{2-}$- 1.0 M NaClO$_4$- 0.027 M TTA +
0.028 M TOPO in toluene at 25 ± 1°C

pcH	[HPO$_4{}^{2-}$]$_T$, M	Activity, cpm Org. Phase	Activity, cpm Aq. Phase	D
7.57	0	6617	519	12.80
7.55	1.00e-04	6542	536	12.25
7.52	3.00e-04	6473	549	11.84
7.56	6.00e-04	6381	559	11.45
7.56	9.00e-04	6380	602	10.63
7.60	1.80e-03	6379	682	9.38
7.56	2.40e-03	6352	742	8.59
7.56	3.00e-03	6193	787	7.88

pcH = - log [H$^+$]. The activity of background: 2.0 cpm.

Table 3. Solvent extraction data for the synergistic extraction system of Np(V)-HPO_4^{2-}- 1.0 M $NaClO_4$- 0.027 M TTA + 0.028 M TOPO in toluene at 40 ± 1^oC

pcH	$[H_2PO_4^{2-}]_T$, M	Activity, cpm Org. Phase	Activity, cpm Aq. Phase	D
7.45	0	8790	564	15.59
7.44	3.00e-04	8777	574	15.31
7.40	6.00e-04	8760	586	14.97
7.45	1.30e-03	8637	644	13.42
7.42	1.70e-03	8406	652	12.91
7.47	1.90e-03	8398	660	12.74
7.41	2.10e-03	8344	669	12.48
7.42	2.50e-03	8331	705	11.82

pcH = - log [H$^+$], $H_2PO_4^{2-}]_T$ –total concentration of Na_2HPO_4, the activity of background: 0.5 cpm.

Table 4. Solvent extraction data for the synergistic extraction system of Np(V)-HPO_4^{2-}- 1.0 M $NaClO_4$- 0.027 M TTA + 0.028 M TOPO in toluene at 55 ± 1^oC

pcH	$[H_2PO_4^{2-}]_T$, M	Activity, cpm Org. Phase	Activity, cpm Aq. Phase	D
7.35	0	3423	246	13.99
7.35	6.50e-04	3398	270	12.63
7.35	1.00e-03	3397	272	12.57
7.35	1.40e-03	3391	277	12.29
7.36	1.80e-03	3378	290	11.69
7.36	2.20e-03	3366	303	11.17
7.33	2.60e-03	3347	322	10.45
7.36	3.10e-03	3339	329	10.18

pcH = - log [H$^+$], $H_2PO_4^{2-}]_T$ –total concentration of Na_2HPO_4, the activity of background: 1.3 cpm

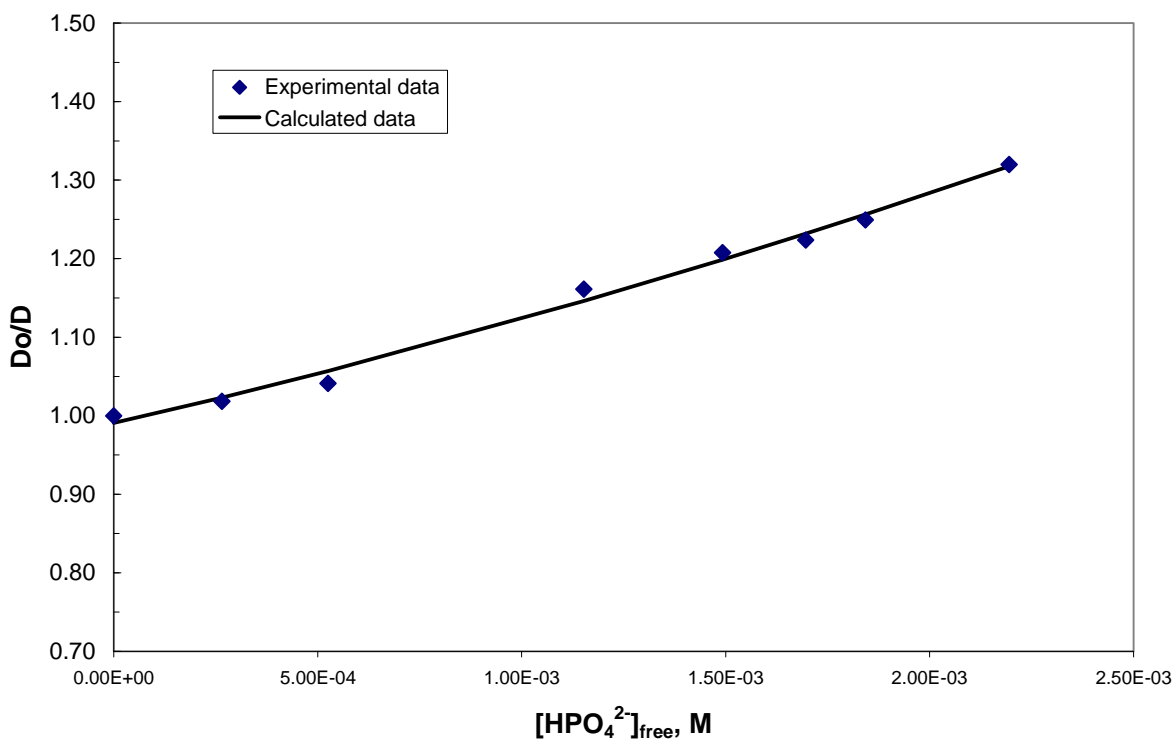**Figure 1. Plot of Do/D vs. concentrations of phosphate in the synergistic extraction system of Np(V)-1.0 M NaClO4-0.027 M TTA+0.028 M TOPO in toluene at 40°C**

Table 5. Apparent stability constants for Np(V) phosphate complexes including literature data

Method	Ionic medium	Temperature, (^{o}C)	log β_{101}	log β_{102}	Reference
$NpO_2^+ + H_2PO_4^- = NpO_2H_2PO_4$ (aq)					
dis	1.0 M NaClO$_4$	25	1.04±0.18		7
dis	1.0 M NaClO$_4$	25	1.18±0.10		21
dis	1.0 M NaClO$_4$	40	1.39±0.06		21
dis	1.0 M NaClO$_4$	55	1.63±0.03		21
$NpO_2^+ + HPO_4^{2-} = NpO_2HPO_4^-$					
cix	0.2 M NH$_4$ClO$_4$	20	2.85±0.15		5
cppt	1 M NH$_4$Cl	20	2.9±0.1		8
cix	0.1 M NaClO$_4$	10	3.11±0.19		6
cix	0.1 M NaClO$_4$	25	2.36±0.42		6
cix	0.1 M NaClO$_4$	35	2.06±0.39		6
dis	1.0 M NaClO$_4$	25	2.11±0.09		7
sp	0.1 M NaClO$_4$	25	2.54±0.02		4
dis	1.0 M NaClO$_4$	25	2.32±0.04		This work
dis	1.0 M NaClO$_4$	40	2.08±0.06		This work
dis	1.0 M NaClO$_4$	55	1.99±0.13		This work
$NpO_2^+ + 2HPO_4^{2-} = NpO_2(HPO_4)_2^{3-}$					
dis	1.0 M NaClO$_4$	25		3.43±0.16	7
dis	1.0 M NaClO$_4$	25		3.78±0.35	This work
dis	1.0 M NaClO$_4$	40		4.14±0.25	This work
dis	1.0 M NaClO$_4$	55		4.22±0.24	This work

Dis: solvent extraction; cix: ion exchange; cppt: co-precipitation method ; sp: spectrophotometric method.

Table 6. Stability constant and thermodynamic values for 1:1 and 1:2 complexes of Np(V) with HPO_4^{2-}

Temperature ^oC	Ionic strength M	$\log \beta_{101}$	$\log \beta_{102}$	$\Delta G^{o'}$ kJ/mol	$\Delta S^{o'}$ J/K mol	$\Delta H^{o'}$ kJ/mol	Reference
For the complex formation of $NpO_2^+ + HPO_4^{2-} = NpO_2HPO_4^-$							
25	1.0	2.32±0.04		-13.25	-25.14	-20.74	this work
40	1.0	2.08±0.06		-12.47	-26.40	-20.74	this work
55	1.0	1.99±0.13		-12.50	-25.10	-20.74	this work
For the complex formation of $NpO_2^+ + 2HPO_4^{2-} = NpO_2HPO_4^{3-}$							
25	1.0		3.78±0.35	-21.56	165.41	27.73	this work
40	1.0		4.14±0.25	-24.63	167.85	27.73	this work
55	1.0		4.22±0.24	-26.52	165.33	27.73	this work